

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Production of Organo-Silicon Compounds

- We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the production of silanes and siloxanes containing quaternary ammonium groups.
- A wide variety of organosilicon compounds and compositions have been prepared and used in many applications because of their useful and advantageous properties. While many of these are of considerable value there are applications where the inclusion of additional or special groups would render them even more valuable. Such groups which can be included to enhance the properties of silanes and siloxanes are the quaternary ammonium groups. In fact, it has been proposed to produce such materials, for example, in British Patent Specification 882,053, by reacting an alkyl halide with an organosilicon compound containing an aminocalkylsilyl group in which the amino groups are separated from the nearest silicon atom by a methylene chain having at least three carbon atoms.
- According to the present invention a process for the production of silanes and siloxanes containing a quaternary ammonium group comprises reacting together a tertiary amine and a halogen-containing silane or siloxane in which the halogen atom or atoms is or are separated from the nearest silicon atom by not less than three carbon atoms.
- Tertiary amines which may be used in the process of our invention include those in which the three groups attached to the nitrogen atom are the same or different and are alkyl, aryl, aralkyl or substituted alkyl, aryl or aralkyl groups, for example, such as trimethylamine, triethylamine, phenyldimethylamine, phenylethyldimethylamine, chlorophenyldimethylamine and  $\gamma$ -chlorobutyldiphenylamine; those in which the nitrogen atom is part of a non-aromatic heterocyclic molecule such as N,N'-ethanopiperazine and N-methylpiperidine; and those in which the nitrogen atom is part of an aromatic heterocyclic structure such as pyridine, pyridazine, pyrimidine, and pyrazine or of a substituted aromatic heterocyclic structure such as bis-(trimethylsiloxy)methylsilyl - ethyl -  $z$  - pico - line.
- Silanes and siloxanes which may be used in the process of our invention preferably have at least one  $\gamma$ -halo-alkyl group and include the silanes having the general formula  $R^1_a R^2_b SiX_{(4-a-b)}$  where  $R^1$  is a  $\gamma$ -halo-alkyl group having at least three carbon atoms and preferably being a  $\gamma$ -chloropropyl group,  $R^2$  is a hydrogen atom or a monovalent hydrocarbon group or halogenated derivative thereof,  $X$  is a halogen atom or an alkoxy, aryloxy or acyloxy group, 'a' is 1, 2, 3 or 4, b is 0, 1, 2 or 3 and a + b is not greater than 4 and siloxanes such as linear polysiloxanes, cyclic polysiloxanes, and cross-linked polysiloxanes in which there is present at least one  $\gamma$ -halo-alkyl group having at least three carbon atoms. In these siloxanes the groups other than the halo-alkyl groups may vary widely and may be the same or different. It is also normally preferred that the ratio of halo-alkyl groups to the other groups in the siloxanes should be from 1:1 to 1:20. Groups which may be present include, for example, alkyl groups such as ethyl and methyl groups, aryl groups such as phenyl groups and alkenyl

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groups such as vinyl and allyl groups. The products obtained from linear siloxanes are preferred for many purposes as they can more easily be used to get products of higher molecular weights. The process of preparing siloxanes according to our invention includes that in which there is first prepared a hydrolysable silane containing the desired quaternary group or groups.

The reaction between the halo-silicon compounds and the tertiary amine may be carried out by heating at elevated temperatures at atmospheric, sub-atmospheric, or at super-atmospheric pressure. A solvent may be used if desired. Suitable solvents include aliphatic and aromatic hydrocarbons, ethers and alcohols, for example, n-heptane, benzene, toluene, benzyl alcohol and di(2-methoxyethyl) ether. The reaction may conveniently be carried out at temperatures of up to about 400°C but is preferably carried out within the range from about 25°C to about 150°C.

The products obtained by the process of our invention are of value in a number of applications where siloxanes have hitherto been used, for example, antifoam agents and sizes for fibrous glass surfaces. The silanes are also of value as modifying agents in silicone oils, greases, rubbers and resins. Thus, for example, the presence of the quaternary ammonium group confers a certain polarity on the products and thus increases the solvent resistance thereof.

Our invention is further illustrated by the following Examples in which all parts are by weight.

#### EXAMPLE 1

15 parts of  $\gamma$ -chloropropylpentamethyldisiloxane and 15 parts of sodium iodide were heated under reflux for 4 hours in 100 parts of anhydrous acetone. The acetone was removed by evaporation and the white precipitate of sodium chloride and sodium iodide removed by filtration. There was thus obtained 20 parts of a viscous liquid consisting of  $\gamma$ -iodopropylpentamethyldisiloxane and having a boiling point of 82–95°C at 14 mm.Hg. pressure and a refractive index of 1.4464 at 25°C.

10.5 parts of  $\gamma$ -iodopropylpentamethyldisiloxane and 3.5 parts of N,N'-ethanopiperazine were heated together at 150°C for 1½ hours. There was obtained by this means 12 parts of a white solid which was washed several times with dry ether and dried at 70°C. This solid was hygroscopic and water soluble and had a melting point of about 75°C and was of value as a surfactant.

#### EXAMPLE 2

10 parts of  $\gamma$ -iodopropylpentamethyldisiloxane prepared as described in Example 1 were heated with 3 parts of pyridine at a

temperature of 150°C for a period of 1½ hours. There was thus obtained 13 parts of a yellowish viscous oil which solidified on cooling. The resulting solid was washed several times with dry ether to give a material having a melting point of about 50°C. This material had properties similar to the product of Example 1.

#### EXAMPLE 3

120 parts of  $\gamma$ -chloropropyltrimethylchlorosilane and 300 parts of trimethylchlorosilane were mixed together and added to 1000 parts of water with vigorous stirring. The oil which separated was dried over anhydrous sodium sulphate and distilled. 65 parts of this material were obtained on distillation over the temperature range 192 to 194°C and had a refractive index of 1.4210 at 20°C. 10 parts of the  $\gamma$ -chloropropylpentamethyldisiloxane obtained in this manner were mixed with 5 parts of N,N'-ethanopiperazine and the mixture heated at 150°C for 1½ hours. There was thus obtained 15 parts of a creamy white solid which was washed several times with dry ether and dried at 40°C. This material slowly darkened on heating above 140°C and had a melting point greater than 250°C. It was suitable for application as a surfactant.

#### EXAMPLE 4

10 parts of  $\gamma$ -iodopropylpentamethyldisiloxane prepared as described in Example 1 were heated with 11 parts of 4[bis(trimethylsiloxy)methylsilyl]ethyl]- $\alpha$ -pivoline at 220°C for 3 hours. There was thus obtained 21 parts of a dark brown resinous solid having a softening point of approximately 50°C. This material was useful for application as a surfactant.

#### EXAMPLE 5

30 parts of bis( $\gamma$ -chloropropyl)tetramethyldisiloxane were reacted with 36 parts of sodium iodide by boiling for 6 hours in 100 parts of anhydrous acetone. By means of filtration and removal of the acetone there was obtained 48 parts of bis( $\gamma$ -iodopropyl)tetramethyldisiloxane.

20 parts of the bis( $\gamma$ -iodopropyl)tetramethyldisiloxane so prepared and 4 parts of N,N'-ethanopiperazine were heated together for 1 hour at 150°C. There was obtained 24 parts of a white resinous material which was washed with dry ether several times and dried in an oven at 70°C. This material softened slightly at 85°C and melted completely at 203 to 213°C. This material was useful as a surfactant.

#### EXAMPLE 6

10 parts of  $\gamma$ -bromopropylpentamethyldisiloxane and 4 parts of N,N'-ethanopiperazine were heated together for 1 hour at 170°C.

There was obtained by this time 12 parts of a white solid which was washed several times with dry ether and dried at 70°C. This solid was very hygroscopic having no definite melting point, at 150°C the solid appeared to soften and at 230°C charred and darkened. This material was useful as a surfactant.

#### EXAMPLE 7

15 parts of  $\gamma$ -chloropropylpentamethyldisiloxane and 5 parts of 4,4'-dipyridyl were heated together for 8 hours at 140°C. The product, 19 parts of a dark brown liquid, which solidified on cooling, dissolved in 50 parts of chloroform and the chloroform evaporated off to yield a viscous dark brown solid. This material was useful as a surfactant.

#### EXAMPLE 8

2.8 parts of  $\gamma$ -bromopropylpentamethyldisiloxane and 1 part of pyridine were heated together for 12 hours at 160°C. Excess pyridine was removed by distillation and there was thus obtained 3.5 parts of a dark brown solid of low melting point. This material was useful as a surfactant.

#### EXAMPLE 9

100 parts of a linear dimethylpolysiloxane end-stopped with a trimethylsilyl group and a  $\gamma$ -chloropropyltrimethylsilyl group and having 20 silicon atoms in the chain and 7 parts of N,N'-ethanopiperazine were heated together for 14 hours between 150 and 180°C under anhydrous conditions. There was thus obtained 106 parts of a light buff coloured liquid giving a slight increase in viscosity to that of the original siloxane liquid. This material was useful as a surfactant.

#### EXAMPLE 10

100 parts of a polysiloxane similar to that used in Example 9 except that it had 40 silicon atoms in the chain and had a  $\gamma$ -chloropropyl group attached to each terminal silicon atom and 4 parts of N,N'-ethanopiperazine were heated for 14 hours between 150 to 180°C. There was thus obtained a dark brown liquid which was much more viscous than the starting siloxane oil. On cooling this liquid 103 parts of a gelatinous brown mass were obtained. This material was insoluble in water, methyl alcohol, ethyl acetate, ether, acetone and toluene but soluble in chloroform. The product was useful as a lubricant and for treatment of glass surfaces.

#### EXAMPLE 11

100 parts of a polysiloxane similar to that used in Example 10 except that it had 80 silicon atoms in the chain and 1.9 parts of N,N'-ethanopiperazine were heated for 80 hours in the presence of 100 parts of toluene. On distilling off the toluene 101.9 parts of a

very viscous liquid was obtained being soluble in benzene, toluene and chloroform. This material was useful as a lubricant and for treatment of glass surfaces.

#### EXAMPLE 12

100 parts of a polysiloxane similar to that used in Example 10 except that it had 60 silicon atoms in the chain and 0.95 parts of N,N'-ethanopiperazine were heated together for 18 hours in the presence of 100 parts of toluene. On distilling off the toluene 100.9 parts of a very viscous liquid was obtained. This was soluble in toluene, benzene and chloroform and was useful as a lubricant and for treatment of glass surfaces.

#### EXAMPLE 13

17 parts of  $\gamma$ -chloropropyltrimethylchlorosilane and 7.9 parts of pyridine were heated together in anhydrous conditions for 6 hours at 130°C. On cooling, two layers were observed both being liquid, the top layer was removed and found to be mainly unreacted pyridine and chlorosilane. The bottom layer at this point solidified, this solid was washed several times in dry ether and finally 25 parts of it isolated as a light brown solid. The product was useful for treatment of glass surfaces.

#### WHAT WE CLAIM IS:—

1. A process for the production of silanes and siloxanes containing a quaternary ammonium group comprising reacting together a tertiary amine and a halogen-containing silane or siloxane in which the halogen atom or atoms is or are searated from the nearest silicon atom by not less than three carbon atoms.
2. A process according to Claim 1 wherein the groups attached to the nitrogen atom of the tertiary amine are alkyl, aryl, alkaryl or substituted alkyl, aryl or alkaryl groups.
3. A process according to Claim 2 wherein the tertiary amine is trimethylamine, triethylamine, phenyldimethylamine, phenylethyldimethylamine, a chlorophenyldimethylamine or  $\gamma$ -chlorobutyldiphenylamine.
4. A process according to Claim 2 wherein the tertiary amine is N,N'-ethanopiperazine or N-methylpiperidine.
5. A process according to Claim 2 wherein the tertiary amine is pyridine, pyridazine, pyrimidine, pyrazine or bis(trimethylsiloxy)methylsilylethyl- $\alpha$ -picoline.
6. A process according to any of the preceding claims wherein the silane or siloxane contains at least one  $\gamma$ -halo-alkyl group.
7. A process according to any of the preceding claims wherein a silane is used which has the general formula  $R^1_nR_bSiX_{(4-a-b)}$  where  $R^1$  is a  $\gamma$ -halo-alkyl group having at least three carbon atoms, R is a hydrogen atom, a monovalent hydrocarbon group or a

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- monovalent halogenated hydrocarbon group, X is a halogen atom or an alkoxy, aroxy or acyloxy group, 'a' is 1, 2, 3 or 4, b is 0, 1, 2 or 3 and a + b is not greater than 4.
- 5 8. A process according to any of the preceding claims wherein the halo-alkyl group is a  $\gamma$ -chloropropyl group.
9. A process according to any of Claims 1 to 6 and 8 wherein a linear, cyclic or cross-linked polysiloxane is used.
- 10 10. A process according to Claim 9 wherein the ratio of halo-alkyl groups to other groups in the siloxane is from 1:1 to 1:20.
11. A process according to any of the preceding claims wherein the silane or siloxane contains, in addition to the halo-alkyl group, alkyl, aryl or alkenyl groups.
- 15 12. A process according to Claim 11 wherein the groups other than halo-alkyl groups are methyl, ethyl, phenyl, vinyl or allyl groups.
- 20 13. A process according to any of the preceding claims wherein the reaction is carried out in presence of a solvent.
- 25 14. A process according to Claim 13 wherein the solvent is n-heptane, benzene, toluene, benzyl alcohol or di(2-methoxyethyl) ether.
15. A process according to any of the preceding claims wherein the reaction is carried out at a temperature of up to about 400°C.
- 30 16. A process according to Claim 15 wherein the temperature is from about 25 to about 150°C.
17. A process for the production of silanes and siloxanes containing quaternary ammonium groups substantially as hereinbefore described and with particular reference to the foregoing Examples.
- 35 18. Silanes and siloxanes whenever produced by a process claimed in any of Claims 1 to 17.
- 40 19. The production of siloxanes containing quaternary ammonium groups by hydrolysing a hydrolysable silane claimed in Claim 18.
- 45 20. Siloxanes containing quaternary ammonium groups whenever produced by the process claimed in Claim 19.
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